

ACETYLATED CASEIN FIBER

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MILLIONS of pounds of casein fiber have been produced, both here and abroad. The fiber is in an active stage of development, as shown by the extensive literature. Compared with wool, casein fiber as ordinarily hardened with formaldehyde is inferior because of its lower tensile strength, particularly when wet, and because of its poor resistance to boiling, especially in mildly alkaline solution. Similar properties with consequent need of improvement have been encountered in artificial fibers prepared from a number of other proteins.

A British patent (14) reported that treating fibers spun from peanut protein with acyl chlorides would improve the resistance of the fiber to hot dilute acid as well as impart water-repellent properties. Reaction with ketene and acetic anhydride was subsequently claimed (15) to produce the same benefits in artificial protein fibers. Another patent (16) deals specifically with the acetylation of casein fiber by ketene or acetic anhydride, with or without catalysts. A process for treating protein fiber such as wool, involving the use of acylating agents like ketene and acetic anhydride in the presence of fatty acid catalysts, to improve or modify dyeing affinities, resistance to water, and other properties, was patented (1). The water-resistant properties and dyeing characteristics of Aralac, the casein fiber made commercially in

this country, were described (9). Up to the present, however, no detailed study of the acylation of hardened casein fiber has been published.

Acetic anhydride has been used to acetylate wool for the purpose of masking the basic groups and thus decreasing the affinity of the wool for acid dyes (4). Elliott and Speakman (3) recently described such a process based on treatment with acetic anhydride and glacial acetic acid in the presence of sulfuric acid. Kise and Carr (7) studied the acetylation of silk fibroin with ketene. Up to 7.3% acetyl content was obtained, depending on the duration of exposure to ketene, but the fibers were colored tan to brown. No correlation with other physical properties was reported. In a later paper, describing the acetylation of silk by acetic anhydride, Carr (2) showed that sodium acetate accelerated the reaction. The literature on the acetylation of proteins other than fibers is reviewed in another article (5).

The investigation reported here was undertaken for the purpose of correlating acetylation with its effect on important properties of casein fiber.

Three types of casein fiber were prepared. All were spun from the same batch of casein. One type was precipitated in a bath containing aluminum sulfate and collected in skein form (referred

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Casein fiber as ordinarily hardened with formaldehyde is inferior to wool as a textile fiber because of its lower tensile strength, especially when wet, and because of its poor resistance to boiling, particularly in mildly alkaline solutions. Claims have been made that acetylation improves some of the inferior properties of protein fiber. No quantitative report on this problem has appeared, so an investigation was made with casein fiber prepared in this Laboratory. Acetylation was carried out with acetic anhydride under various conditions, including the presence of catalysts. Acetyl contents from 1.0 to 9.0% were obtained by varying the time and temperature. Correlations between acetyl content and various properties are reported. Acetyl contents of about 6% could be introduced with no loss of wet or dry tensile strength. Fibers of such acetyl content are superior to the untreated control fiber in regard to resistance to boiling solutions simulating dye-bath conditions. They also have the desirable property of a greatly decreased affinity for acid dyes—i.e., dyes with colored anions—and thus more closely approximate wool in dye uptake.

to as aluminum skein fiber); another was precipitated in the same bath and collected on reels (aluminum reel fiber); and the third type was precipitated in a bath free of aluminum salts and collected on reels (non-aluminum reel fiber). The fiber collected on reels was under tension during hardening with formaldehyde; that collected in skein form was not hardened under tension. The spinning solution contained 21.5% casein (calculated on the dry basis) and 0.92% sodium hydroxide; the pH was 9.6 to 9.8. This solution was held for 16 hours at 55° C. The material was spun through a 500-hole tantalum spinnerette into a 40-liter bath containing 10% by weight of sulfuric acid, 14% of sodium sulfate, 7.9% of aluminum sulfate octadecahydrate, and 100 cc. of 37% formaldehyde. The bath was replenished with salts, acid, and formaldehyde as needed to maintain its original composition. In the preparation of the nonaluminum fibers, an equivalent amount of sodium sulfate was substituted in the bath for the aluminum salt. The skeins or reels, weighing 80 to 100 grams net, were hardened for 16 hours in a solution containing 30% of sodium acetate trihydrate and 5% of formaldehyde, adjusted to pH 5.5 by addition of acetic acid. They were then washed thoroughly and dried at room temperature. After being removed from the reels, the fibers were thoroughly washed again and dried at room temperature.

The fibers were prepared according to a simplified formula¹ to yield uniform batches of base fiber. Neither maximal tensile strength nor pronounced resistance to boiling solutions was sought, since it was desired to give full range to the effects of acetylation on these properties. Casein fibers with considerably higher tensile strengths and with greater resistance to boiling than the control fiber used in the present investigation have been made in this Laboratory¹.

¹ The preparation of fiber of greater tenacity as well as further details of procedures employed for spinning and testing will be described in a later paper from this Laboratory.

PREPARATION. Three flasks equipped with reflux condensers each containing 175 cc. of acetic anhydride, were placed large oil bath kept at constant temperature. When the desired temperature had been reached, 10-gram samples of each of the three types of fiber (conditioned at room atmosphere) were immersed in the anhydride. The large excess of anhydride was used to make sure that all the fiber was covered and thus uniformly treated. After the desired heating period the anhydride was decanted; the fibers were removed, washed in a pan of running tap water for 20 minutes, and then steeped in a pan of warm water at 55–60° C. for 20 minutes to exhaust the anhydride. The fibers were whirled in a small basket centrifuge and allowed to dry in air. In each case the treated fiber was compared with the untreated fiber of the skein or reel from which it was taken.

ANALYSIS. Moisture determinations were run simultaneously with the analyses for ash and acetyl, which are tabulated on a moisture-free basis. Moisture content was determined on a 0.1–0.2 gram sample by drying to constant weight in a vacuum oven at 70° C. for 16 to 18 hours. Acetyl content was determined by the method of Hendrix and Paquin (6). Before analysis all samples were extracted in a Soxhlet apparatus with acetone. To retain acetic acid, a little aqueous sodium hydroxide was added to the solvent in the boiling flask. Total ash was run essentially according to the calcium acetate method as described by Sutermeister and Browne (13). The properties of the treated samples, together with the conditions of preparation, are shown in Table I.

TABLE I. PREPARATION AND PROPERTIES OF ACETYLATED FIBER

Sample No. ^a	Heating Period, Hr.	Temp., °C.	Acetyl Content, %	Total Ash Content, %	% Water after Im-mersion	Tensile Strength, Gram/Denier		Color of Acetylated Fiber
						Dry	Wet	
A. Nonaluminum Reel								
1-1 ^b	32.1	0.62	0.18	White
2-1	0.5	60	1.2	2.36	31.8	0.58	0.17	White
3-1	1.5	60	1.1	2.43	31.2	0.60	0.17	White
4-1	3.0	60	1.2	2.20	30.7	0.58	0.16	White
5-1	6.0	60	1.7	2.28	27.4	0.59	0.16	White
6-1	0.5	80	1.7	2.12	29.1	0.60	0.15	White
7-1	1.5	80	3.7	2.10	31.2	0.57	0.17	White
8-3	3.0	80	5.6	2.02	28.9	0.55	0.18	White
9-1	6.0	80	6.4	2.15	28.9	0.64	0.22	White
10-3 ^b	2.36	35.7	0.60	0.16	White
11-3	0.5	100	5.3	1.97	25.9	0.62	0.18	White
12-3	1.0	100	6.3	1.83	25.1	0.59	0.15	White
13-3	1.5	100	6.5	1.99	24.0	0.63	0.17	Cream
14-3	2.0	100	7.2	2.18	23.5	0.63	0.21	Cream
15-3	4.0	100	7.6	2.02	25.7	0.60	0.21	Light tan
16-3	0.5	110	6.4	2.07	26.8	0.60	0.18	Cream
17-3	1.5	110	7.4	2.23	28.7	0.58	0.18	Light tan
18-3	3.0	110	8.1	2.37	26.7	0.54	0.23	Tan
19-8 ^b	35.0	0.60	0.15	White
20-8	0.5	120	6.7	1.96	23.4	0.58	0.18	Cream
21-8	1.5	120	8.7	1.99	22.3	0.46	0.15	Tan
22-8	3.0	120	9.0	1.94	21.1	0.46	0.14	Dark tan
B. Aluminum Reel								
1-1 ^b	4.59	41.3	0.58	0.17	White
2-1	0.5	60	1.0	4.28	40.6	0.60	0.18	White
3-1	1.5	60	1.2	4.69	38.9	0.59	0.16	White
4-1	3.0	60	1.2	4.27	37.0	0.57	0.17	White
5-1	6.0	60	1.3	4.10	36.0	0.62	0.17	White
6-1	0.5	80	1.6	4.62	38.7	0.60	0.17	White
7-1	1.5	80	2.0	4.00	37.7	0.63	0.19	White
8-1	3.0	80	2.3	4.08	36.7	0.68	0.21	White
9-1	6.0	80	5.4	4.72	35.0	0.63	0.22	White
10-2 ^b	5.08	41.3	0.59	0.24	White
11-2	0.5	100	3.5	4.66	34.5	0.65	0.22	White
12-2	1.0	100	5.2	4.89	34.2	0.66	0.22	White
13-2	1.5	100	5.7	4.86	35.3	0.66	0.23	Cream
14-2	2.0	100	5.8	5.06	33.6	0.65	0.25	Cream
15-2	4.0	100	6.0	4.90	33.1	0.64	0.22	Light tan
16-2	0.5	110	4.5	5.03	32.0	0.66	0.22	Cream
17-2	1.5	110	6.3	4.92	31.3	0.62	0.24	Light tan
18-2	3.0	110	7.1	4.93	29.1	0.63	0.22	Tan
19-8 ^b	41.5	0.59	0.19	White
20-2	0.5	120	5.7	5.01	30.9	0.60	0.22	Cream
21-8	1.5	120	7.2	5.02	32.9	0.57	0.18	Tan
22-8	3.0	120	8.2	4.94	28.8	0.51	0.17	Dark tan

^a Number following dash indicates reel from which sample was prepared.

^b Untreated control.

A complete set of data comparable to those presented in Table I^a for the aluminum reel fiber was obtained with the aluminum n fiber, but since it led to the same conclusions, it is omitted.

EFFECT OF TIME, TEMPERATURE, AND CATALYSTS

The data in Table I show the effects of time and temperature on acetylation. Increasing the time of reaction increased the amount of acetyl introduced at any given temperature, although the value finally leveled off. The effect of temperature was marked, as summarized by the data in Table II. Above 80° C. the rate of acetylation increased rapidly with temperature. It is important from a practical standpoint that the acetylation process shall not color the fiber; this coloration may occur when it is necessary to employ the vigorous treatment required to introduce 6% or more of the acetyl group. Any colors imparted to the fibers by the acetylation treatment are listed in Table I.

The uniformly higher total ash contents of the aluminum fibers indicate that the aluminum retained from the precipitating bath was not lost in the acetylation treatment. The nitrogen content of these fibers was not determined, but in preliminary experiments (not tabulated here) it decreased in proportion to the increase in acetylation.

Some idea of the distribution of the acetyl groups in typical derivatives was obtained by treating the fibers with dilute alkali. It is well known that *O*-acetyl groups are alkali labile (11). Samples (0.5 gram) of the ground fiber were treated with 25 cc. of 0.1 *N* sodium hydroxide at room temperature for 6 hours, and the filtrates were analyzed for acetic acid. Acetyl in excess of 2.0 to 2.5% was removed by this treatment, an indication that much of the acetyl of highly acetylated casein fiber is of the alkali-labile type. This is also true for nonfibrous casein derivatives (5, 6). In contrast to this lability, acetylglycine and acetylsarcosine are not attacked under the same conditions after 48 hours.

Since acetylation may be accelerated by either acidic or basic catalysts, the effects of various catalysts were studied. Table III lists the details of the experiments. Acid catalysts did not increase the degree of acetylation in any case. Addition of acetic acid alone had almost no effect. For this reason air-dried sam-

ples can be used directly for acetylation without concern for acetic acid generated from small amounts of water and acetic anhydride. Basic catalysts, on the other hand, increased the amount of acetylation slightly in every case, but this advantage was offset by the decrease in tensile strength of the fibers so treated.

In connection with the catalytic study, the effect of organic diluents on acetylation was observed. Treatment of the fibers with 5, 10, and 20% solutions of acetic anhydride in benzene for 3 hours under reflux introduced only about 10% of the acetyl groups that were introduced with acetic anhydride alone under the same conditions. If acetic anhydride were used alone in a continuous process, acetic acid would accumulate in the acetylation bath. Since acetic acid has little effect on acetylation, the bath could be periodically replenished—for example, by reconverting the acetic acid to the anhydride with ketene.

EFFECT OF ACETYLATION ON TENSILE STRENGTH

For tensile strength measurements the fibers were conditioned for 24 hours in a room kept at 65% relative humidity and 70° F. (21° C.). Tensile strength was determined on a Scott tester. Each value is the mean of results on at least ten bundles. According to this method as applied to our fiber series, a difference greater than 0.03 gram per denier is significant. The washing treatment used to free the acetylated fibers of excess anhydride and acid had no demonstrable effect on the tensile strength of unacetylated fiber.

The data in Table I^a indicate that acetylation of nonaluminum fiber does not increase the dry tensile strength. On the other hand treatment at 100° C. and short treatment at higher temperatures introduced a high acetyl content without decreasing the tensile strength. Longer treatment at temperatures of 110° C. and higher injured the fiber. Acetylation did not increase the wet tensile strength.

Table I^b shows that acetylation at 100° C. may increase the dry tensile strength of aluminum reel fiber slightly. These fibers did not show the marked decrease in tensile strength exhibited by the nonaluminum fibers after acetylation for longer times at 110° C. or higher. The wet tensile strength of the fibers was not affected by moderate acetylation treatment. From the standpoint of tensile strength, aluminum reel fibers acetylated at 100° C. were consistently best. Since these fibers could be heated for longer periods at 100° C. without decreasing the fiber strength, the safety factor for operation at this temperature is great.

To correlate acetylation and heat treatment (baking) of the fiber with tensile strength, the aluminum and nonaluminum reel fibers described in Table I were studied. The results are shown in Table IV. All acetylations were performed at 100° C. for 1 hour.

It is clear that baking, as carried out in these experiments, has no effect on tensile strength.

TABLE II. EFFECT OF TEMPERATURE ON ACETYLATION^a

Temp., ° C.	Acetyl Content, %			
	Nonaluminum reel fiber		Aluminum reel fiber	
	0.5 hr.	1.5 hr.	0.5 hr.	1.5 hr.
60	1.2	1.1	1.0	1.2
80	1.7	3.7	1.6	2.0
100	5.3	6.5	3.5	5.7
110	6.4	7.4	4.5	6.3
120	6.7	8.7	5.7	7.2

^a The fibers were prepared by heating in acetic anhydride, as described previously.

TABLE III. EFFECT OF ACIDIC AND BASIC CATALYSTS ON ACETYLATION

Catalyst Used	Weight of Catalyst, Grams	Acetic Anhydride, Cc. ^a	Heating Period, Hr.	Temp., ° C.	Acetyl Content, %	Tensile Strength, Gram/Denier	
						Dry	Wet
None	...	200	3.0	85	2.5	0.61 ^b	0.22 ^b
<i>p</i> -Toluenesulfonic acid	0.3	200	3.2	85	1.4	0.56	0.17
Concd. H ₂ SO ₄	0.9	200	3.2	85	1.3	0.59	0.19
Zinc chloride	0.4	200	3.2	85	1.0	0.52	0.23
Magnesium perchlorate	0.4	200	3.2	85	1.6	0.61	0.17
None	0.56	0.18
Concd. H ₂ SO ₄	0.2	100	1	100	6.6	0.50 ^c	0.22 ^c
Stearic acid	5	100	1	100	5.9	0.54	0.22
Acetic acid	21	95	1	100	6.4	0.50	0.24
Anhydrous sodium acetate	5 ^d	80	1	100	6.2	0.47	0.22
and acetic acid	10 ^e	85	1	100	7.6	0.46	0.19
Same	5	50	1	100	6.9	0.41	0.18
Anhydrous sodium acetate	10	95	1	100	7.8	0.36	0.16
and acetic acid	10	90	1	100	7.2	0.44	0.19
None	0.46	0.18

^a 5 grams of aluminum skein fiber used in each case.

^b Value for untreated fiber from which next five samples were obtained.

^c Value for untreated fiber from which remaining samples were obtained.

^d 10 cc. of glacial acetic acid used to dissolve sodium acetate.

^e 50 cc. of glacial acetic acid used.

WATER CONTENT AND DEGREE OF ACETYLATION

The water-binding capacity of cellulose is progressively decreased by acetylation of its hydroxyl groups (12). Recently the decreased uptake of water by acylated casein plastics was demonstrated (5). To show the effect of acetylation on the water absorption of fibers, their water contents after soaking in water were determined by a modification of the method of McMeekin and Warner (8) for the water content of β -lactoglobulin crystals. A 20–30 mg. sample of fiber, previously extracted with acetone and dried at room temperature, was soaked for 1 hour in 5 cc. of twice-distilled water in a test tube maintained at 25° C. At the end of this period the sample of fiber was removed and immediately pressed between

TABLE IV. EFFECT OF ACETYLATION AND BAKING ON TENSILE STRENGTH

Treatment	Tensile Strength, Gram/Denier			
	Nonaluminum reel fiber ^a		Aluminum reel fiber ^a	
	Dry	Wet	Dry	Wet
Untreated	0.64	0.21	0.60	0.19
Baked ^b	0.62	0.24	0.60	0.20
Acetylated	0.60	0.18	0.62	0.20
Acetylated, then baked ^b	0.63	0.21	0.62	0.20

^a Fibers were all taken from the same reel.

^b Samples were baked at 120° C. for 3 hours.

TABLE V. EFFECT OF BOILING FOR ONE HOUR IN SOLUTIONS OF DIFFERENT pH VALUES ON APPEARANCE AND FEEL^a OF NONALUMINUM REEL FIBER

pH ^b	Untreated Fiber	Fiber of Low Acetyl Content (1.2%)	Fiber of High Acetyl Content (6.3%)
2.9	Disintegrated	Very brittle; hard	Normal
4.1	Very hard lump	Brittle	Normal
5.1	Very hard lump	Very brittle	Normal
6.1	Disintegrated	Brittle; powdered	Normal
7.1	Disintegrated	Hard brittle mass	Normal
8.0	Disintegrated	Hard brittle mass	Powdered when rubbed
8.5	Disintegrated	Hard brittle mass	Powdered badly when rubbed

^a Fibers were allowed to dry at room temperature.

^b Citrate-phosphate buffers were used for pH 2.9, 4.1, 5.1, and 6.1; phosphate buffer for pH 7.1; and borax-borate buffer for pH 8.0 and 8.5.

TABLE VI. EFFECT OF DEGREE OF ACETYLATION ON DYE UPTAKE^a

Acetyl, %	Aluminum Reel Fiber		Acetyl, %	Nonaluminum Reel Fiber	
	Dye exhaust, %			Dye exhaust, %	
	Calcomine ^b	Pontamine ^c		Calcomine ^b	Pontamine ^c
0.0	97.0	Exhausted	0.0	81.7	88.5
1.2	56.3	99.4	1.1	30.0	59.6
2.3	13.8	38.1	3.7	14.4	20.3
3.5	11.1	24.3	5.3	10.8	18.5
4.5	8.1	9.4	6.5	10.0	12.6
5.8	7.6	8.3	7.6	9.5	11.4
7.1	6.8	7.1	8.7	7.6	7.1
8.2	3.0	3.0			

^a 0.2 gram of fiber was boiled in 100 cc. of dye solution at pH 4.5 for 5 minutes; the concentration of dye remaining in solution was determined by photoelectric colorimetry.

^b Calcomine Fast Red 8B; 100 cc. of dye solution contained 37.5 mg. dye and 10 cc. of 0.2 M acetate buffer.

^c Pontamine Fast Blue RRL; 100 cc. of dye solution contained 10.0 mg. dye and 10 cc. of 0.2 M acetate buffer.

blotters, the time being recorded by a stop watch (zero time). The fiber was pressed twice more to ensure removal of adhering water, and was weighed as soon as possible (usually within 60 seconds) on a tared watch glass with a Chainomatic analytical balance. At the instant the weight was determined to the nearest 0.1 mg., the time which had elapsed since zero time was recorded. The drying fiber was allowed to remain on the balance pan, and successive 0.5-mg. losses in weight were accurately timed until three such pairs of figures were recorded. By plotting weight against time and extrapolating to zero time, the wet weight of the fiber on removal from the water was obtained. The sample was then dried to constant weight at 105° C., and the percentage of water in the wet fiber was calculated. Average values of at least two determinations, expressed as water content after immersion, are shown in Table I. The deviation of measured values from their average in no case exceeded 3% of this mean.

Distilled water rather than buffer solutions was chosen because the values obtained for water content after immersion in the latter were much higher. For example, after a representative acetylated fiber was immersed in 1/15 M phosphate buffer of pH 7.0, the water content was 54.1%, in contrast to 31.8% after immersion in water. The values in Table IA indicate that nonaluminum fibers of low acetyl percentage had a water content up to 3% less than the untreated material, whereas the water contents of highly acetylated fibers were decreased by about 7 to 14%. The same correlation of decreased water content with increased acetyl content was also evident with buffered solutions in place

of distilled water. The untreated aluminum reel fiber had a water content about 7% higher than the untreated nonaluminum fiber, probably owing to the water uptake by the inorganic matter. The values in Table IB, compared with those in I, show that the decrease in water content with increase of acetylation is not so great as with the nonaluminum fibers. This difference is not surprising in view of the larger ash content of the aluminum fiber.

CORRELATION OF RESISTANCE TO BOILING WITH DEGREE OF ACETYLATION

When formaldehyde-hardened casein fiber is boiled for an hour, the material becomes gelatinous and weak, the extent of change depending on the pH of the medium (10). A boiling test simulating dye-bath conditions was used in order to correlate resistance to boiling with degree of acetylation. For the test, 0.1 gram of the fiber was boiled in 25 cc. of the buffer solution under reflux for 1 hour. The sample was then removed, examined, pressed between blotters, and dried at room temperature. The choice of buffers did not seem to influence the results at any given pH.

To study the effect of pH, boiling tests were carried out at various pH values with the acetylated nonaluminum reel fibers described in Table IA. The appearance and feel of the fibers after the boiling tests are described in Table V. The differences in resistance were marked. These results have been duplicated many times. At all pH values other than 4 and 5, the untreated materials became gelatinous and disintegrated. At pH 4 and 5, however, a hard mass devoid of all fibrous structure resulted on drying. In contrast to the untreated fiber, the fiber of 1.2% acetyl content did not disintegrate at any pH value listed but became brittle when dry. This fiber was most resistant at pH 4 to 6. The fiber of 6.3% acetyl content was extremely resistant over the pH range 2.9 to 7.0, and appeared normal after drying but at higher pH values this fiber powdered somewhat when dry and rubbed. When the three samples were boiled in distilled water, the results were substantially the same as when they were boiled in buffer solutions of pH 5 to 6.

Boiling tests at different pH values were also made with the aluminum fibers of 0, 1.0, and 5.2% acetyl content described in Table IB. The effects of pH were the same as those with the nonaluminum fibers. In general, however, observation of the results of many experiments showed that the acetylated fiber containing aluminum salt was more resistant to boiling and did not feel so harsh after the boiling treatment.

DYE UPTAKE AND ACETYL CONTENT

Much has been written about the extreme affinity of casein fiber for dyes, and acetylation has been advocated as a method of reducing the dye affinity of casein fiber to approximately that of wool (1). With a series of fibers of increasing acetyl content, the relation was easily demonstrated. Results with two types of fibers and with two different dyes are shown in Table VI. Since the pH of the dyeing solution has such a marked influence on dye uptake, preliminary tests were made to obtain a dyeing rate slow enough to permit comparisons between the entire set of acetylated samples. With both the dyes used, a pH of 4.5 was satisfactory. All the results make apparent the decrease in dye affinity with increased acetyl content. The large decrease in percentage dye exhaust with introduction of small amounts of acetyl can be explained by the initial action of acetylation treatment, mainly, masking of the basic groups. Thus the protein groups responsible for combining with most of the colored anion of the dye at this pH can be masked by relatively little acetylation. That these are not the only groups participating is evident from the fact that acetylation over and above that necessary to cover the basic groups still decreased the dye uptake. From these results it also seems that the nonaluminum fiber takes up less dye than the aluminum fiber of similar acetyl content.

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